STUDIES ON THE CONSTITUENTS OF THE VOLATILE OIL FROM THE LEAF OF *CHAMAECYPARIS OBTUSA*, SIEB. ET ZUCC., F. *FORMOSANA*, HAYATA, OR ARISAN-HINOKI. PART II.

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In the previous paper, the authors and C. Hata have reported on the terpenic as well as the terpenic alcoholic constituents of the essential oil from the leaf of "arisan-hinoki" or *chamaecyparis obtusa*, Sieb. et Zucc. f. *formosana*, Hayata.[1] The present paper is its sequel and deals with the higher boiling ingredients of the same. As regards the high-boiling constituents of similar essential oils, R. Tsuchihashi and S. Tasaki[2] have reported that cadinene and a dicyclic sesquiterpene alcohol-chamaecypariol were present in the wood oil from the same plant as the authors', while S. Uchida,[3] who examined the leaf oil of "hinoki" or Japanese *chamaecyparis*, has proved, besides cadinene, a tricyclic sesquiterpene, a dicyclic sesquiterpene alcohol, and an inactive tetracyclic diterpene in it. The present authors' oil, however, showed a marked difference from the foregoing in various respects, a brief account of which will be described first.

The authors' sesquiterpene fraction, which occupied about 38% by weight of the whole oil, consisted for the most part of three sesquiterpenes, among which the most predominating was a new tricyclic sesquiterpene, the rest represent *d*-cadinene and another tricyclic sesquiterpene. The name "sesquichamene" is suggested by the authors to this predominant tricyclic sesquiterpene. From point of view of physical constants, sesquichamene is almost identical with many of the hitherto known sesquiterpenes of the tricyclic class, such as cedrene,[4] tricyclogurjunene,[5] or longifolene,[6] but it differs decidedly from the others in many chemical behaviours. The most characteristic of all is that it gives a crystalline nitrosochloride which melts with decomposition at 78°-79°C. It is rather unstable and cannot be kept for more than a few hours even in the purest state, but, unstable as it is, it should be remarked, that this is the only crystalline nitrosochloride ever prepared out of tricyclic sesquiterpenses. The nitrolbenzylamine can also be prepared from this nitrosochloride. It

(1) This Bulletin, **6** (1931), 40.
(2) *Report of Govern. Research Inst. Formosa* (1920).
(3) *J. Soc. Chem. Ind. Japan*, **19** (1916), 611.
(4) Semmler, *Ber.*, **40** (1907), 3521; **45** (1912), 355.
5) Semmler, *Ber.*, **47** (1914), 1029, 1141.
6) Simonsen, *J. Chem. Soc*, **117** (1920), 570; **123** (1923), 2642.

melts at 158°-159°C. The nitrosochloride dissolves readily in chloroform and acetone forming blue solutions, from which the original nitrosochloride can be reprecipitated by the addition of ethyl or methyl alcohol, and thus it can be purified by repeating this treatment. It should be remembered, however, that the nitrosochloride is also very unstable in the dissolved state, and the blue colour of the solutions rapidly fades away into yellow minute by minute, and once it becomes yellow, then the reprecipitation impossible.

Sesquichamene slowly oxidizes in the air, and the yield of the characteristic nitrosochloride is maximal only directly after its distillation but declines steadily and ultimately into nil on standing. By oxidizing sesquichamene with potassium permanganate in acetone solution, a glycol melting at 89°-91°. a diketone whose disemicarbazone melting with decomposition at 233°, and a crystalline substance of an undefined nature, have been obtained. By the action of alcoholic sulphuric acid, sesquichamene undergoes isomerization and gives rise to an isomer which should be named "isosesquichamene." Isosesquichamene has a far lower rotatory power and a greater stability than the original sesquichamene. It should be noted that in our sesquiterpene fraction, a small quantity of isosesquichamene was found to be present. Whether this sesquiterpene had been present in the original oil, or had it arisen from sesquichamene during the processes of fractional distillations, remains to be discussed later. Uchida's tricyclic sesquiterpene also seems possibly to be the same, but in his case, it is to be anticipated that it resulted from sesquichamene by the action of heat, as his fractionations were carried out under the atmospheric pressure. Table 1 shows the physical constants and the melting points of characteristic derivatives of hitherto known tricyclic sesquiterpenes and those of sesquichamene and isosesquichamene:

Table 1.

	Cedrene	Tricyclogurjunene	Longifolene
	(Semmler)[4]	(Semmler)[5]	(Simonsen)[6]
B. p.	121°—124°/12	120°—123°/13	150°—151°/35
d	0.9354/15	0.9348/15	0.9284/30
n_D	1.5030	1.5028	1.495/30
α_D	−56° (86°)	+74.5°	+42.7°
Hydrochloride	liq.	liq.	59°—60°
Ketone $C_{15}H_{24}O$	43°	43°	....
Semicarbazone	242°—243°	237°	....
Diketone	....	....	94°—95°
Disemicarbazone	234°	....	....
Glycol	168° (172°)	....	....
Nitrosochloride	....	....	....
Nitrolbenzylamine	....	....	....

Table 1.—(*Concluded*)

	Sesquichamene (Authors')	Isosesquichamene (Authors')	Isosesquichamene[3] (Uchida)
B. p.	$122°-123°/_{12}$	$129°-131°/_{12}$	$265°-268°/_{760}$
d	$0.9277/_{28}$	$0.9320/_{20}$	$0.9367/_{20}$
n_D	$1.5012/_{28}$	$1.5109/_{21}$	$1.5009/_{20}$
α_D	$-89.4°/_{28}$	$-8.5°/_{21}$	$-15.7°$ (alcohol)
Hydrochloride	liq.	liq.	liq.
Ketone $C_{15}H_{24}O$	....	....	....
Semicarbazone	....	....	....
Diketone	....	....	....
Disemicarbazone	233° (dec.)	....	....
Glycol	89°—91° (dec.)	....	....
Nitrosochloride	78°—79° (dec.)	....	....
Nitrolbenzylamine	165°—166° (dec.)	....	....

The sesquiterpene alcohol fraction amounted to about 8% of the whole oil and contained a dextro-rotatory dicyclic sesquiterpene alcohol and cadinol. Besides, it contained also a very small quantity of tricyclic sesquiterpene alcohol which was not cedrol. The dicyclic sesquiterpene alcohol present was probably identical with that which had been found by Uchida in Japanese chamaecyparis oil. The only definitely identified compound among these was cadinol.

The diterpene fraction was very poor, amounting to only 1% of the original oil. Its physical properties showed that it consisted mainly of a laevo-rotatory tetracyclic diterpene. Its rotatory power, however, on treatment with acids, or by the action of heat, went diminutive and gave rise to an inactive diterpene which was most probably identical with Uchida's inactive diterpene in the above-mentioned oil. We wish to propose the name "chamaecyparene" to this active diterpene, and also the name "isochamaecyparene" to the racemized or isomerized inactive diterpene. The following table shows the physical properties of the dicyclic sesquiterpene alcohol and the diterpene obtained by Uchida and by us:

Table 2.

	Sesquiterpene Alcohol		Diterpene	
	(Uchida)	(Authors')	(Uchida)	(Authors')
B. p.	$290°-295°/_{760}$	$146°-148°/_{12}$	$340°-343°/_{760}$	$185°-186°/_{12}$
d	$0.9599/_{4}$	$0.9492/_{25}$	$0.9624/_{15}$	$0.9648/_{25}$
n_D	$1.5020/_{20}$	$1.4995/_{25}$	$1.5190/_{20}$	$1.5158/_{25}$
α_D	$+18°$ (alcoh.)	$+4.0°$	$\pm 0°$	$-25.1°$

Experimental.

The Sesquiterpene Fraction. After eight consecutive systematic fractional distillations under 12 mm. pressure (the last three times over metallic sodium) the following eleven fractions were obtained:—

	B. p. / 12 mm.	Distillate	n_D^{25}	d_4^{25}	α_D^{25}	M. R.
(1)	115°–120°	10	1.4940	0.9240	−37.0°	64.27
(2)	120°–122°	34	1.4990	0.9272	−51.8°	64.60
(3)	122°–124°	467	1.5031	0.9297	−85.8°	64.87
(4)	124°–126°	57	1.5035	0.9283	−70.6°	65.01
(5)	126°–128°	14	1.5048	0.9274	−52.8°	65.22
(6)	123°–130°	8	1.5049	0.9261	−31.5°	65.32
(7)	130°–132°	31	1.5062	0.9244	−13.7°	65.59
(8)	132°–134°	24	1.5075	0.9232	+18.0°	65.59
(9)	134°–136°	68	1.5073	0.9226	+43.1°	65.84
(10)	136°–140°	23	1.5056	0.9238	+44.2°	65.56
(11)	140°–142°	18	1.5024	....	+14.0°	....

A glance at these constants enables us to notice that the main constituent is represented by the fraction (3) where a preponderating maximum of the quantity of distillate as well as maxima of density and laevo-rotation are to be observed. From considerations of the molecular refraction it is evident that the predominant sesquiterpene belongs to the tricyclic class. The fraction (9) is also peculiar, corresponding to a small maximum of the quantity of distillate, a minimum of density, and a maximum of the dextro-rotation. This fraction should represent a dicyclic sesquiterpene as its molecular refraction is much greater than that of the fraction (3).

Sesquichamene. On rectification of the fraction (3), its physical constants exhibited the following values:

B. p. 122.5°–123.5° / 12 mm.; n_D^{28} 1.5021; d_4^{28} 0.9277; α_D^{28} −89.85°;

M. R. found 64.81, calculated as $C_{15}H_{24}$ 64.45;

Anal. Subst. = 0.1627; CO_2 = 0.5254; H_2O = 0.1687 gr. Found: C = 88.01; H = 11.52%. Calc. for $C_{15}H_{24}$: C = 88.16; H = 11.84%.

Sesquichamene Nitrosochloride. A pure, freshly distilled sesquichamene was dissolved in twice its volume of absolute ether, and a current of

dry nitrosyl chloride gas was passed through the cold solution contained in a vessel surrounded by freezing mixtures. After a while, the vessel became filled with crystals. The vessel was left in the cold for half an hour more, and then the crystals were filtered, washed with cold ether and alcohol, and dried in vacuo. The yield of this crystalline substance amounted to about 75-80%. It was then purified by reprecipitating its chloroformic solution with methyl alcohol, and was obtained as colourless needles melting with methyl alcohol, and was obtained as colourless needles melting with decomposition at 77.5°-78.5°. A very pure sample obtained by repeating this process several times, could be kept for three to five hours without any appreciable decomposition. It is very soluble in chloroform and benzol, pretty soluble in petroleum ether, ethyl acetate, aceton, and ether, but very slightly so in methyl alcohol, ethyl alcohol, and water.

Sesquichamene Nitrolbenzylamine. A weighed quantity of the nitrosochloride was suspended in a small volume of alcohol to which a slight excess of an alcoholic solution of benzylamine was slowly added in the cold. The crystals of the nitrosochloride was seen to disappear gradually as the temperature of the solution reached the room temperature, and then the product of reaction was precipitated by adding water thereto, filtered, washed with ether, and recrystallized from dilute alcohol. Sesquichamene nitrolbenzylamine thus prepared melted with decomposition at 165°-166°.

By the action of sodium nitrite and glacial acetic acid on sesquichamene, a semicrystalline deposit of sesquichamene nitrosite was obtained, but no further means of purification was possible as the crude nitrosite, on dissolving it in any of the ordinary solvents, was liable to pass into the oily state never to crystallize again. The preparation of the nitrosate was also tried but with negative results.

Oxidation of Sesquichamene. A mixture of 40 gr. of sesquichamene, 250 gr. acetone, and 80 c.c. of water was put into a vessel and kept agitated. To this mixture 80 gr. of finely powdered potassium permanganate was added in small portions, the temperature being kept under 40° the while. In half an hour the reaction was over, so the solution was filtered, the precipitate of manganese dioxide thoroughly extracted with hot acetone, the acetone solutions combined, evaporated, and then the whole mass was subjected to steam distillation. Nextly the products of reaction were divided into an acidic and a neutral portions in the usual manner.

The neutral products were collected and they were fractionated by three successive fractional distillations, when the fractions with following properties came over :—

	B. p.	Pressure	gr.	n_D^{28}	α_D^{28}
(1)	up to 140°	12 mm.	5	1.5140	− 80.0°
(2)	140°—155°	,,	2	1.5067	....
(3)	155°—160°	,,	7	1.5028	−89.3°
(4)	160°—165°	,,	11	1.5040	−79.3°
(5)	165°—170°	,,	1	1.5044	....
(6)	170°—175°	,,	2	1.5059	....
(7)	175°—180°	,,	1	1.5068	....
(8)	161°—163°	4 mm.	26	1.5090	−21.3°

The residue from these distillations represented a solid mass, which when extracted with acetone while hot, left a white powder. This powder was soluble in chloroform and benzol, but insoluble in alcohol, acetone, or ethyl acetate. The chloroformic solution, on addition of methyl alcohol, deposited an oil which solidified in course of time but looked possibly amorphous. It sintered at 220° and melted with decomposition at 240°-245°.

The fraction (8) on standing gave a little crystalline deposit which could not be separated from its mother liquor by ordinary filtration on account of its excessive viscidness. Therefore, it was dissolved in 3-5 volumes of petroleum ether and kept still for a length of time in the ice box, until at last an aggregation of fine needle crystals separated out. It was filtered and washed with ice-cold petroleum ether, and then recrystallized from hot petroleum benzine. It melted at 89°-91°.

Anal. Subst. = 3.333 mg.; CO_2 = 9.20 mg.; H_2O = 3.311 mg. Found: C = 75.35; H = 11.12%. Calc. for $C_{15}H_{26}O_2$: C = 75.6; H = 10.9%.

The fractions (3) to (8) were treated with solutions of sodium acetate and semicarbazide hydrochloride and the crystalline deposit formed thereby filtered, washed with alcohol and ether, and dried. From each of the fractions the same semicarbazone resulted which melted with decomposition at 233°. It differed from hydrazodicarbonamide (m.p. 257°) in being insoluble in all ordinary organic solvents and also in its crystalline form and solubility in hot water. The result of analysis is as follows :—

1.89 mg. substance gave 0.414 c.c. nitrogen (23.5°C; 765.4 mm.).

	Found	$C_{17}H_{30}O_2N_6$	$C_{17}H_{28}O_2N_6$	$C_{16}H_{28}O_2N_6$	$C_{16}H_{26}O_2N_6$
N%:	24.9	24.0	24.1	25.0	25.2

It follows that the substance in question was either a semicarbazide-semicarbazone of an unsaturated monoketone $C_{14}H_{20}O$ or a disemicarbazone of a diketone $C_{14}H_{20}O_2$. But since this substance was not soluble in mineral acids, it is to be expected that this substance represents a disemicarbazone of a diketone or a keto-aldehyde.

Isosesquichamene. Shaking with aqueous sulphuric acid brought no action on sesquichamene, but when alcoholic sulphuric acid was used, its optical activity gradually demolished. Thus, 25 gr. sesquichamene was treated with 10 gr. of alcoholic sulphuric acid (1:1) at 40°-50°, when in course of 1.5 hours its activity depressed to the value -9.5°. It was then twice rectified over metallic sodium and a main fraction with the following properties was obtained :—

B. p. 129°—131° / 12 mm.; $n_D^{21.5}$ 1.5109; $d_4^{21.5}$ 0.9320; $\alpha_D^{21.5}$ −8.52°;

M. R. Found : 65.60. Calc. : 64.79 as $C_{15}H_{24}\overline{|}_1$; 65.60 as $C_{15}H_{24}\overline{|}_2$.

This sesquiterpene showed a fairly more stable quality against the action of the air but afforded no crystalline hydrochloride by treatment with hydrogen chloride gas.

d-Cadinene. The fractions (9) and (10) when dissolved in twice the volume of absolute ether, treated with a current of dry hydrogen chloride gas, and kept in cold for two days, deposited a quantity of needle crystals on evaporating off ether. After recrystallization from alcohol these crystals melted at 118°-119°, and were proved to be identical with cadinene dihydrochloride, as they showed no depression of the melting point on admixture with pure cadinene dihydrochloride from known source. From these fractions no nitrosite, nitrosate or nitrosochloride could be obtained in the crystalline state.

The fraction (7) gave neither hydrochloride nor nitrosochloride on usual treatment. Judging from its physical constants it seems most probable that it contained isosesquichamene.

The Sesquiterpene Alcohol and Diterpene Fractions. The portion containing sesquiterpene alcohols and diterpenes was fractionated six times under 12 mm. pressure and separated into the following eleven fractions, the physical constants of which are tabulated below :—

	B. p. / 12 mm.	Distillate	n_D^{25}	d_4^{25}	α_D^{25}
(1)	136°—140°	17 gr.	1.5018	0.9388	+14.8°
(2)	140°—145°	23	1.5006	....	+ 8.3°
(3)	145°—149°	55	1.5001	0.9482	+ 3.5°
(4)	149°—151°	15	1.5021	....	+ 5.6°
(5)	151°—154°	35	1.5033	0.9680	+ 7.8°
(6)	154°—157°	39	1.5062	0.9773	+ 8.8°
(7)	157°—159°	11	1.5113	0.9824	− 5.3°
(8)	159°—163°	23	1.5130	0.9860	−10.4°
(9)	163°—170°	5	1.5170	....	−20.0°
(10)	170°—180°	11	1.5184	....	−23.6°
(11)	180°—186°	22	1.5185	0.9650	−22.8°

d-Cadinol. On rectification the fractions (5) and (6) gave a main part having the following characteristics:

B. p. 146°—148°/12 mm.; $n_D^{22.5}$ 1.5043; $d_4^{22.5}$ 0.9706; α_D^{22} +7.76°;
M. R. Found: 67.91. Calc. as $C_{15}H_{26}O$ 68.12.

By the action of hydrogen chloride, cadinene dihydrochloride melting at 118°-119° resulted, which showed no depression of melting point on mixing it with a pure specimen obtained from known sources. This fraction gave no other characteristic derivatives.

From considerations of physical properties, the fraction (3) and (8) seemed likely to consist of sesquiterpene alcohols of dicyclic and tricyclic structure respectively, but all attempts to get definite proofs failed.

The fraction (11) was further rectified in vacuo and a main fraction consisting chiefly of diterpenes was obtained. It showed the following constants:—

B. p. 185°—186°/12 mm.; n_D^{25} 1.5185; d_4^{25} 0.9648; α_D^{25} −25.1°;
M. R. Found: 85.56. Calc. as $C_{20}H_{32}\equiv_1$ 85.21.

On treatment with alcoholic sulphuric acid (1:1), the optical activity of the diterpene enfeebled pretty rapidly. Also on heating it to 350° for several hours inactiviation ensued.

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DENSITIES OF ISOPROPYL AND n-BUTYL ALCOHOLS AT LOW TEMPERATURES.

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Densities of isopropyl- and n-butyl alcohols were determined with the pycnometers made of pyrex glass as shown in Fig. 1. The pycnometer has a bulb of about 3.5 c.c. capacity which is connected to a capillary tube, whose inner diameter is 0.2 cm. and whose length 20 cm. Two marks (a and b) were etched on the capillary tube.

Fig. 1.

The volumes of the pycnometers are calibrated with mercury according to the method proposed by K. Issac and I. Masson.[1] The schematic diagram of the calibration apparatus is shown in Fig. 2. The pycnometer, mounted vertically in a water jacket kept at constant temperature, is connected to a two way capillary stopcock (A), one way of which is connected through a trap (B) to a mercury diffusion pump, by which the pycnometer can be evacuated. When the pycnometer has been completely exhausted, the stopcock (A) is turned 180° and the mercury in the cup (D) is allowed to enter in it by the other way of the stopcock. The cup (D), which is to be taken out and weighed, is placed in a bottle with a rubber stopper (E), so that the cup can be kept free from all dirty substances that may prevent accurate weighing. By means of the glass tube (C) with two stopcocks, one being connected to a pump and the other to atmosphere, the pressure of the bottle is regulated in order that the mercury in the pycnometer is allowed down to an appropriate position, say a. The volume of the bulb is thus determined by the difference of the weight of mercury in D before and after emptying the pycnometer with mercury. The total volume and the volume of the every cm. of the capillary tube between the marks a and b are similarly determined. In all cases the height of the meniscus of mercury and the mark a or b are read by a cathetometer. With the data thus obtained the correction for the capillary at the position l cm. from the mark a is calculated and plotted against l.

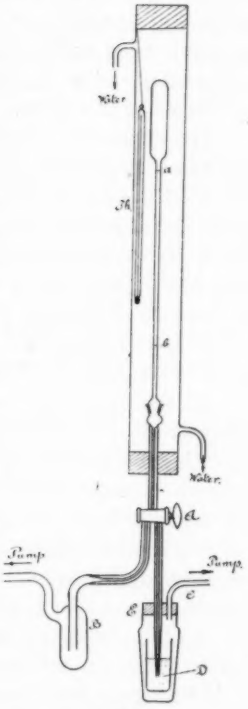

Fig. 2.

After the pycnometer has been allowed to cool several times to the temperature of liquid air, its volume is again determined. It is thus ascertained that the hysteresis of volume change of pycnometer is negligibly small. (The difference of volume before and after is 1 parts in 15000.)

(1) *J. Phys. Chem.*, **28** (1924), 166.

The volume of the sample filled in the pycnometer at the temperature t is calculated as follows.

$$V = V_0(1-3\alpha t)+vl(1-2\alpha t)+\Delta v_I+\Delta v_{II} \quad \ldots\ldots\ldots \quad (1)$$

where V_0 is the volume of bulb at 0°, v, the mean volume of the capillary tube per cm., l, the distance between a and the meniscus of the liquid filled in the pycnometer, Δv_I, the above mentioned correction of volume of the capillary tube at the position l, Δv_{II}, the correction of volume of the meniscus given in the Int. Nat. Crit. Table, Vol. 1, p. 73., α, the expansion coefficient of the glass.

The expansion coefficient α of the glass is determined, by using ethyl ether as a standard. Ether is filled in the pycnometer as described below and with the aid of formula (1), neglecting the expansion coefficient of the glass, the apparent volumes at several temperatures of ether are calculated. The true volumes of ether at corresponding temperatures are calculated from the data given by Keyes and Felsing.[1] From the differences between the true and apparent volumes of ether, the contraction of the pycnometer is calculated, assuming the contraction to be linear to temperature. The linear expansion coefficient of the glass thus found is 5.1×10^{-7}.

All the materials used for the present experiments are Kahlbaum extra pure chemicals. After dehydrating by anhydrous calcium oxide, they have the following boiling point: isopropyl alcohol, 81.9°–82.4°/768.6 mm., corr. and red. b.p.=81.9°C; n-butyl alcohol, 116.7°–117.0°/757.0 mm., corr. and red. b.p.=117.0.

The loading apparatus of the sample is shown in Fig. 3. It is made of ordinary glass except the portion below D, which is made of pyrex glass and they are sealed together at D with pyrex-ordinary glass graded sealing. The sample loads first in A, removes any gases dissolved by evacuation, distills twice at ordinary temperature under vaccum using liquid air as cooling reagent for condenser. Each time first and last one fourth of distillate are rejected. When the proper quantities of the sample have condensed in the pycnometers, they are sealed off at a. The pycnometers with sample are then immersed vertically in the cryostat.

The cryostat is constructed according to R. Hara and H. Shinozaki[2] and its temperature is kept constant within 0.05°. Its temperature is determined by a platinum-resistance thermometer from Leeds and Northrup Co., which has been calibrated at the normal boiling point of oxygen (-182.97°), the normal sublimation point of carbon dioxide (-78.5), the ice point and

(1) *J. Am. Chem. Soc.*, **41** (1919), 589.
(2) *J. Soc. Chem. Ind. of Japan*, **29** (1926), 269.

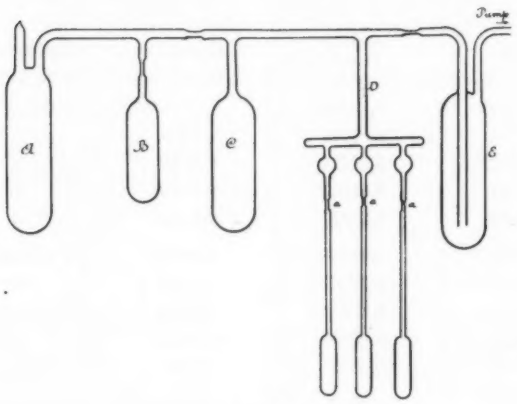

Fig. 3.

boiling point of water. It has the resistance of 2.5089 (r_0) at 0° and the resistance (r) at any temperature t is calculated by the following formula.

$$r/r_0=1+3.97186\cdot10^{-3}t+6.148\cdot10^{-7}t^2+5.08\cdot10^{-12}t^4 \quad . \quad . \quad . \quad (2)$$

Cylindrical Dewar vessel of the cryostat is silvered except the spaces of about 1 cm. wide along the mother line of the vessel, through which the meniscus of the pycnometer is observed from outside by a cathetometer, so as to calculate the volume of the sample in the pycnometer by the formula (1).

The densities at each temperature can be expressed by

$$D=w/V \quad . \quad . \quad .

Table 1. Densities of Isopropyl-alcohol.

Temp.	Density (obs.)	D (calc.)	Pycnometer
− 0.00	0.80430		5, 6 and 8
− 7.02	0.81083	0.81005	6
− 10.02	0.81234	0.81243	6
− 10.26	0.81293	0.81256	1
− 10.57	0.81376	0.81295	6
− 17.17	0.81884	0.81834	1 and 6
− 20.77	0.82167	0.82127	6
− 28.09	0.82742	0.82723	2 and 5
− 41.85	0.83855	0.83840	6
− 43.75	0.83938	0.83991	2 and 5
− 44.25	0.84037	0.84031	1 and 6
− 54.17	0.84810	0.84831	2 and 5
− 54.95	0.84869	0.84894	1 and 6
− 65.80	0.85723	0.85762	5
− 76.80	0.86603	0.86645	5
− 90.82	0.87725	0.87762	1 and 6
−106.03	0.89030	0.89967	6

Table 2. Densities of n-Butyl-alcohol.

Temp.	Density	D (calc.)	Pycnometer
0.00	0.82380		2, 2, 5 and 8
−11.28	0.83264	0.83259	2, 5 and 6
−18.14	0.83852	0.83831	5 and 6
−23.30	0.84197	0.84193	2 and 6
−32.87	0.84936	0.84934	2 and 6
−37.70	0.85305	0.85307	2 and 6
−38.36	0.85349	0.85358	2 and 6
−39.45	0.85448	0.85442	2 and 6
−45.70	0.85932	0.85923	2 and 6
−55.33	0.86654	0.86662	2 and 6
−55.44	0.86676	0.86671	2 and 6
−69.06	0.87729	0.87701	2 and 6
−75.58	0.88241	0.88211	2 and 6
−80.80	0.88607	0.88607	2 and 6

and for n-butyl-alcohol,

$$D=0.82380-0.0007819\,t-0.000000129\,t^2$$

Table 3 contains the calculated densities from the above formulae at temperature of round numbers.

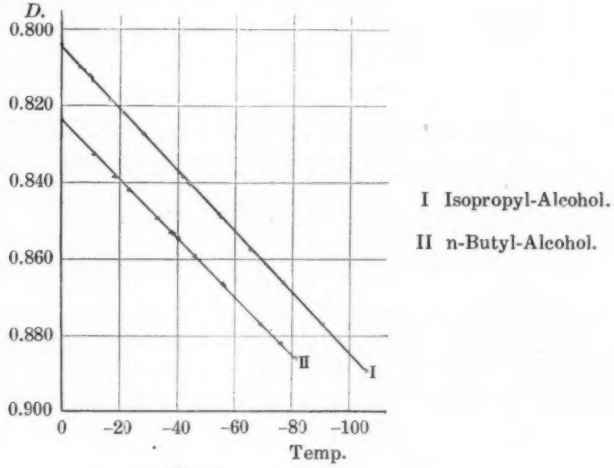

Fig. 4.

Table 3. Densities of Isopropyl-and n-Butyl-alcohol.

Temp.	Isopropyl-alcohol	n-Butyl-alcohol	Temp.	Isopropyl-alcohol	n-Butyl-alcohol
0.00	0.80430	0.82380	— 50.00	0.84179	0.86258
— 5.00	0.80836	0.82771	— 55.00	0.84516	0.86642
— 10.00	0.81236	0.83161	— 60.00	0.84845	0.87025
— 15.00	0.81628	0.83550	— 65.00	0.85167	0.87407
— 20.00	0.82014	0.83939	— 70.00	0.85482	0.87790
— 25.00	0.82392	0.84327	— 75.00	0.85790	0.88171
— 30.00	0.82764	0.84714	— 80.00	0.86091	0.88552
— 35.00	0.83128	0.85101	— 85.00	0.86389	
— 40.00	0.83486	0.85487	— 90.00	0.86672	
— 45.00	0.83837	0.85873	— 95.00	0.86953	
			—100.00	0.87226	
			—105.00	0.87401	

In conclusion, the present authors acknowledge the helpful guidance of Prof. S. Mitsukuri, who also kindly paid a part of the expenses of the experiments from the research fund granted to him from the Imperial Academy and from the Saito Gratitude Foundation.

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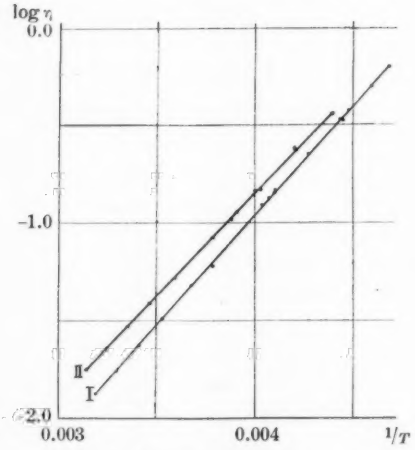
VISCOSITIES OF ISOPROPYL AND n-BUTYL ALCOHOLS AT LOW TEMPERATURES.

By Tokuzô TONOMURA.

Received April 4th, 1931. Published May 28th, 1931.

The viscosities of isopropyl- and n-butyl alcohols at low temperatures were determined by the present author with the modified Ostwald's viscosimeters that were reported in the previous papers.[1], [2] The results were summarized in Tables 1 and 2, and shown in the accompanying figure. The



I Isopropyl-Alcohol.
II n-Butyl-Alcohol.

(1) S. Mitsukuri and T. Tonomura, *J. Chem. Soc. of Japan*, **48** (1927), 335.
(2) S. Mitsukuri and T. Tonomura, Ibid., **50** (1929), 120.

densities of the alcohols were taken from the data given by T. Tonomura and K. Uehara.[1] The constants of the viscosimeters were given in Table 4 of the previous paper.

Table 1.

The Viscosities of Isopropyl-alcohol.

Temp. °C	Density	Time of fall sec.	Viscosity C.G.S.	Viscosimeter
0.00	0.8043	118.10	0.04510	3
− 0.20	0.8045	123.20	0.04706	3
− 6.77	0.8099	155.75	0.05989	3
− 9.38	0.8120	172.30	0.06643	3
−16.32	0.8177	224.58	0.08719	3
−19.15	0.8200	248.40	0.09676	3
−20.40	0.8211	262.83	0.10247	3
−24.07	0.8240	304.47	0.11870	3
−27.48	0.8267	117.74	0.13331	4
−29.29	0.8282	128.57	0.14205	4
−29.50	0.8284	376.29	0.14300	3
−39.14	0.8362	194.47	0.22273	4
−43.80	0.8400	241.17	0.27385	4
−47.36	0.8428	290.35	0.3351	4
−49.83	0.8448	322.43	0.3731	4
−55.33	0.8492	427.77	0.4976	4
−59.83	0.8529	544.30	0.6358	4

Table 2.

The Viscosities of n-Butyl-alcohol.

Temp. °C	Density	Time of fall sec.	Viscosity C.G.S.	Viscosimeter
0.00	0.8238		0.05186	(Thorpe and Rodger)
−14.12	0.8348	211.40	0.08379	3
−20.72	0.8399	90.32	0.10391	4
−22.31	0.8412	281.41	0.11240	3
−22.38	0.8412	95.50	0.11004	4
−29.65	0.8469	124.48	0.14440	4
−30.12	0.8472	126.40	0.14668	4
−40.74	0.8553	199.01	0.23314	4
−40.89	0.8556	197.39	0.23133	4
−50.92	0.8633	305.27	0.36100	4

(1) T. Tonomura and K. Uehara, this Bulletin, **6** (1931), 118.

The relations between the viscosities and the temperatures were expressed by the following formula, where A, B and C were the constants.

$$\log \eta = -A + B/(T-C)$$

The values of the constants were given in the Table 3.

Table 3.

Alcohol	A	B	C
Isopropyl	5.4727	1127.09	0
n-Butyl	5.0562	1051.65	5.2

The author here expresses his gratitude to Prof. S. Mitsukuri, under whose helpful guidance the present experiments were carried out.

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SINOMENINE AND DISINOMENINE. PART XXVI. ON THE DECOMPOSITION OF SINOMENINE WITH DIMETHYL-SULPHATE.

By **Kakuji GOTO** and **Kenjiro TAKUBO.**

Received April 8th, 1931. Published May 28th, 1931.

In the XXV report of this study,[1] the Hofmann decomposition of sinomenine with the use of methyliodide and alkali was reported. In this communication, the same reactions were repeated with dimethylsulphate and alkali, and the results obtained partly ascertained those of the last report, but in regard to the nitrogen free substance, a new diphenanthryl derivative, different from the disinomenol, was obtained. These results are, for brevity's sake, summarized in the following way.

1. Sinomenine metho-sulphate [I] is best obtained by adding dimethylsulphate to the aqueous suspension of sinomenine and by precipitating the metho-sulphate by sodium carbonate solution. In this way, the yield is almost quantitative. The metho-sulphate shows the diazo-, $FeCl_3$, and

(1) This Bulletin, **6** (1931), 79.

$FeK_3(CN)_6 + CO_3Na_2$ reactions just as sinomenine hydrochloride itself and behaves against hot, dilute alkali in the same way as the iodomethylate does.

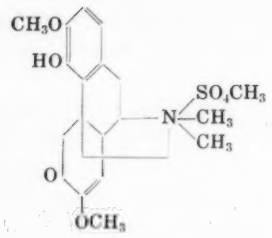
2. When sinomenine is methylated by dimethyl sulphate and caustic alkali at low temperature (cooling with ice-water), methyl-sinomenine metho-sulphate [II] is produced. The success of the reaction depends largely on the condition of the experiment, and the yield is very poor (15%). The trial to prepare this metho-sulphate from methyl-sinomenine in the way given [I] was unsuccessful.

3. The difficulty of the above reaction [2] lies chiefly in the easy opening of C_9–N linking of the metho-sulphate by the caustic alkali at the room temperature. In the latter condition, two kinds of methyl-sinomenine methine metho-sulphates, namely, the methyl-sinomenine-roseomethine-methosulphate and the methyl-sinomenine-violeo-methine-metho-sulphate [III] were isolated. Of these two, the former was more difficulty obtainable and in numerous experiments, it was obtained only twice (yield about 5%). The metho-sulphate of the methyl-sinomenine-violeomethine is, however, obtainable from sinomenine-achro-methine by dimethyl-sulphate and caustic soda at O°C in a yield 60%.

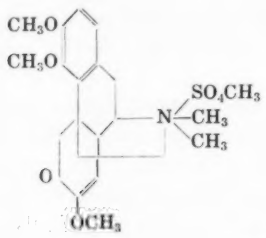
4. When the methyl-sinomenine-violeo-methine metho-sulphate is decomposed by boiling caustic soda (2–25%), a nitrogen-free substance ($C_{24}H_{30}O_8$; m.p. 310°) is produced. From the elemental analysis, the methoxyl content and the molecular weight determination, it must be a double molecular monomethyl-sinomenol. The linking point is supposed to be C_5, adjuscent to the free phenol group, which is newly formed from the original ketone group. The substance is named, therefore, 4,4′-dimethyl-bis-(5,5′)-sinomenol. This point was supported by the fact that the 4,4′, 6,6′-tetramethyl-bis-(5,5′)-sinomenol is quite different from the tetramethyl-disinomenol, obtained from sinomenine or disinomenine by the boiling 66% KOH and the followed methylation.

5. The above tetramethyl-bis-(5,5′)-sinomenol can be obtained directly from sinomenine by dimethyl-sulphate and alkali at the room temperature, if the reaction mixture is kept for a long time. This shows that the methyl-amino-ethyl-side chain of sinomenine is in a condition, which can be easily splitted off in the course of the aromatisation.

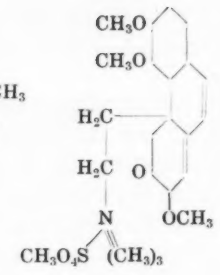
6. When the reaction mixture of sinomenine, dimethyl sulphate and caustic alkali is boiled, then the mixture of dimethyl-sinomenol and tetramethyl-bis-(5′5′)–sinomenol is obtained. This fact shows that there must be produced also the monomolecular 4-methyl-sinomenol, which perhaps on account of its low melting point could not be isolated in crystalline condition up to present.



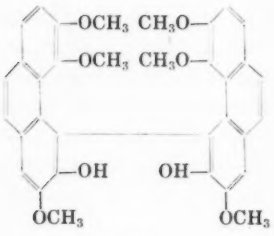
[I]



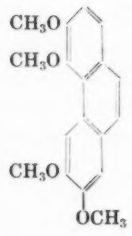
[II]



[III]



[IV]



[V]

7. By the present study, the following change in the nomenclature applied in the preliminary report appeared in *Proc. Imp. Acad.*, 2 (1926), 167 were necessitated.

The new nomenclature	To be abolished
1) Methyl-sinomenine-violeo-methine-metho-sulphate	1) α-Methyl-sinomenine-methine-methyl-sulphate
2) Methyl-sinomenine-roseo-methine-metho-sulphate	2) β-Methyl-sinomenine-methine-methyl-sulphate
3) 4, 4′-Dimethyl-bis-(5, 5′)-sinomenol	3) Trimethoxy-keto-vinyl-phenanthrene-tetrahydride
4) Tetramethyl-bis-(5, 5′)-sinomenol	4) α-Tetramethoxy-vinyl-phenanthrene-dihydride
5) Dimethyl-sinomenol	5) β-Tetramethoxy-vinyl-phenanthrene-dihydride m.p. 122°

Experimental.

1. **Sinomenine-methyl-methosulphate** [I]. Sinomenine hydrochloride (13.3 gr.) in an aqueous solution (80 c.c.) was added with anhydrous sodium carbonate (2 gr), and to this suspension of the free base, dimethyl sulphate

(9 c.c.) was added and well stirred. To the clear solution, which is produced in half an hour, a saturated sodium carbonate solution (40 c.c.) is added. After several hours, the precipitate is collected and recrystallized from ten parts of water. M.p. 265°C (decomposes). Yield quantitative. It gives no halochromy with conc. H_2SO_4 and HCl.

Anal. Found: C = 55.50; H = 6.23; N = 3.05; S = 7.06; CH_3O- = 20.53%.
$C_{21}H_{27}O_8NS$ requires C = 55.48; H = 6.58; N = 3.07; S = 7.03; CH_3O- = 20.39%.

2. Methyl-sinomenine-methyl-metho-sulphate. Sinomenine hydrochloride (10 gr) in an aqueous solution (70 c.c.) was added with anhydrous Na_2CO_3(1.5 gr in 20 c.c. water). This fine suspension of sinomenine was methylated with dimethyl sulphate (30 c.c.) and 33% NaOH (26 c.c.), given alterately in small portions, until the diazo-reaction disappeared. The reaction mixture was then extracted with chloroform sixteen times. By evaporating the dried chloroform, 1.5 gr. of the methyl-sinomenine methosulphate was obtained. It is hygroscopic, but recrystallisable from methanol into colourless prisms, melting at 245°. It gives no reaction for phenol group.

Anal. Found: CH_3O- = 25.89%. 4 CH_3O- in $C_{22}H_{29}O_8NS$ requires CH_3O- = 26.38%.

3. Methyl-sinomenine-violeo-methine-methyl-metho-sulphate [III].

(A) From sinomenine hydrochloride. The condition of the methylation is almost the same as (2), only the reagents being used in a somewhat larger quantity and the reaction mixture was warmed at 45° for some time. After six hours, the mixture was saturated with CO_2, added with Na_2CO_3 (saturated; 20 c.c.) and extracted with chloroform. The methosulphate is then precipitated from the chloroform solution (1 part) by ether (4 parts). Recrystallized from alcohol, it forms beautiful long prisms, which melts and decomposes at 204° sharply.

The substance is, however, better to be prepared from the sinomenine-achro-methine, as follows.

(B) Crude sinomenine-achro-methine (4.5 gr) is dissolved in 10% NaOH (15 c.c.) and set aside for 1.5 hours. (This treatment changes the achromethine into the violeo-methine). Then, the solution is methylated with dimethyl sulphate (15 c.c.) and 30% NaOH (15 c.c.) under ice-cooling. The reaction is completed by letting the mixture stand at the room temperature for three hours.

The yield is 2.5 gr, namely 60% of the theoretical.

The metho-sulphate dissolves deep blue in conc. H_2SO_4 and fuming HCl respectively.

Anal. Found: C = 57.28; H = 6.87; N = 3.02; S = 6.69; CH_3O- = 25.15%. $C_{23}H_{33}O_8SN$ = 483 requires C = 57.14; H = 6.83; N = 3.02; S = 6.63; $CH_3O-(4)$ = 25.67%.

Sp. rotatory power, measured in water,

$$[\alpha]_D^{13} = +(7.14 \div 0.1492) \times (10 \div 1) = +478°$$

Sp. rotatory power, measured in chloroform,

$$[\alpha]_D^{20} = +(5.70 \div 0.245) \times (25 \div 1) = +581.6°$$

4. Methyl-sinomenine-roseo-methine-methyl-methosulphate. Sinomenine (10 gr) was methylated with dimethyl-sulphate (50 c.c.) and 30% NaOH (68 c.c.) in an aqueous suspension (120 c.c.) The solution was nearly neutralized, added with saturated Na_2CO_3 solution (30 c.c.) and boiled for two hours. By extracting the cooled solution with chloroform, a reddish syrup (3.5 gr) was obtained from which on standing long separated first the crystals of methyl-sinomenine-violeo-methine-methyl-metho-sulphate. The alcoholic filtrate therefrom deposited, also on long standing, rhombic plates of the methyl-metho-sulphate of methyl sinomenine-roseo-methine. M.p. 178°. The substance dissolves deep red in conc. H_2SO_4 and in fuming HCl.

Anal. Found: N = 2.99; CH_3O- = 24.38%. Calculated: N = 2.99; $CH_3O-(4)$ = 25.67%.

5. 4,4'-Dimethyl-bis-(5.5')-sinomenol [IV]. Methyl-sinomenine-violeo-methine-methyl-metho-sulphate was boiled with ten times its weight of 2% NaOH for 20 minutes. The amine evolved was absorbed in dilute HCl. The aqueous part was extracted with chloroform, and the residue of the evaporation of the chloroform was recrystallised from glacial acetic acid or chloroform. It forms long colourless prisms, which melt at 310°. Yield ca. 20%. It dissolves in conc. H_2SO_4 brownish, and gives a green precipitate on diluting with water, but it does not show the sinomenol-reaction.

Anal. Found: C = 71.96; H = 5.27; CH_3O- = 32.86%. $C_{34}H_{30}O_8$ = 566
Requires: C = 72.05; H = 5.30; $CH_3O-(6)$ = 32.68%.

Mol. Weight after Rast's,

$$M = (0.263 \div 2.478) \times 100 \times (400 \div 6.3) = 674.$$

The amine evolved was identified as trimethyl amine from the m.p. of its auri-chloride (m.p. 251°) and platini-chloride (m.p. 245°). It is clear that the trimethyl-amine is produced from the $CH_3 \cdot CH_2 \cdot N(CH_3)_3OH$ secondarily.

6. 4,4′-Dimethyl-6,6′-diacetyl-bis-(5,5′)-sinomenol. 4,4′-Dimethyl-bis-(5,5′)-sinomenol [IV] gives this diacetylated substance, when boiled with acetic anhydride, added with Na-acetate for one hour. It is recrystallised from methanol in long prisms, m.p. 230°.

Anal. Found: C = 69.72, 69.85; H = 5.48, 5.52; CH_3O- = 28.63 %. $C_{38}H_{34}O_{10}$ requires: C = 70.15; H = 5.23; $CH_3O-(6)$ = 28.61 %.

7. Tetramethoxy-bis-(5,5′)-sinomenol. (A). Sinomenine HCl (20 gr) was methylated in an aqueous solution (100 c.c.) with dimethyl sulphate (53 c.c.) and 33% NaOH (79 c.c.) On standing this mixture for three weeks, a yellow crystalline substance was deposited on the bottom. The latter was dissolved in chloroform and precipitated with ethyl alcohol into long colourless prisms. M.p. 280°, but the substance recrystallised from acetone (1500 parts) melted at 283°C. Yield ca 2.2 gr. i.e. 13% of the theoretical.

(B). As the above preparation requires much time, it is better to boil the filtrate of the preparation, described in [3, B] with 33% NaOH (7 c.c.). As this filtrate contains some methyl-sinomenine-metho-sulphate and Na-CH_3-sulphate, so it gives tetramethyl-bis-(5,5′)-sinomenol in a tolerably good yield.

The substance is easily soluble in chloroform but very difficulty in alcohol, acetone (1:1 500) and ether. It dissolves in conc. H_2SO_4 brown and gives a green precipitate on diluting with water. Very resistent against $KMnO_4$. It has no rotatory power, showing that the sidechain must have been splitt off completely.

Anal. Found: C = 72.55, 72.34; H = 5.81, 6.18; CH_3O- = 41.64 %. $C_{36}H_{34}O_8$ = 594 requires: C = 72.46; H = 5.79; $CH_3O-(8)$ = 41.75 %.

Mol. Weight after Rast's,

$$M = (0.227 \div 2.142) \times 100 \times (400 \div 6.1) = 695.$$

Sp. rotatory power, measured in chloroform,

$$[\alpha]_D^{18} = (0 \div 0.1057) \times (10 \div 1) = 0.$$

8. In the preparation of 7, (A), we obtain a mixture of dimethyl-sinomenol and tetramethyl-bis-(5,5′)-sinomenol in different proportions,

when we boil the methylating mixture, using the dimethyl-sulphate and cautic alkali in different proportions. This shows that there must be the formation of the monomolecular 4-methyl-sinomenol in the above treatment, but the latter is not obtained in crystalline form yet. The substance, given in Proc. Imp. Acad. 2, (1926) 169, as β-tetramethoxy-vinyl-phenanthrene-dihydride (m.p. 122°), turned out to be nothing but dimethyl-sinomenol itself. The analysis made clear this point.

Anal. Found: C=72.38, 72.34; H=6.38, 6.18%. Calc. for $C_{18}H_{18}O_4$: C=72.45; H = 6.08%.

9. Dimethyl-sinomenol chinone. The alkaline filtrate from the preparation 7, (A), was diluted and oxidised with a dilute $KMnO_4$ solution, so long as the latter is still decolourised. Ether extracts therefrom a deep red substance (prisms) in a minute quantity. It melts at 266°C and forms a phenazine, which melts at 184°C. The mixed m.p. showed the substance is dimethyl-sinomenol-chinone, reported already in this Bulletin 4 (1929), 169.

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